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Abstract. GEMS are to the outer solar system what chondrules are to the inner solar system. Ten years after it was first proposed that GEMS are the long-sought interstellar amorphous silicates, ion microprobe measurements have confirmed that some of them are indeed interstellar amorphous silicates. The new challenges are to obtain even higher precision isotope measurements from these submicrometer-sized objects and to clarify how and where they originally formed. Individual GEMS exhibit a strikingly narrow (0.1-0.5 μm diameter) size distribution and they are systematically depleted from solar abundances in S/Si, Mg/Si, Ca/Si and Fe/Si, implying that they formed by a common mechanism. Mineralogical and petrographic evidence suggest that irradiation processing may be that mechanism. Recent nanometer-scale compositional mapping using new-generation transmission electron microscopes reveals that truly pristine GEMS may be relatively rare and new metrics need to be developed to distinguish the primordial properties of GEMS from more recent secondary alteration effects.

Introduction: Like chondrules, GEMS (glass with embedded metal and sulfides) are enigmatic objects preserving a cosmochemical record of fundamental relevance to meteoritics, cosmochemistry, and planetary science. Unlike chondrules, GEMS may not have formed in the solar system but, irrespective of where they formed, they are the most abundant silicates in most anhydrous chondritic porous (CP) interplanetary dust particles (IDPs), some or all which may be from comets (Bradley 2004; Brownlee et al. 1995). These submicrometer-sized spheroids (Figs. 1, 2, 5) are mostly composed of nanometer-sized (1-20 nm) FeNi metal and FeNi-sulfide crystals embedded in Mg-rich silicate glass. They typically have bulk compositions that are approximately (within a factor of three) chondritic for the major elements (Westphal & Bradley 2004). Their glassy silicate matrices are consistent with the ~10 µm interstellar "silicate" feature and nanometer-sized superparamagnetic (FeNi metal) inclusions within GEMS can explain the observed magnetic alignment of interstellar silicates within the weak galactic magnetic field. The exotic properties of GEMS appear to be unique among known terrestrial and extraterrestrial geological materials.

The mineralogical, physical, and optical properties of GEMS are similar to those of interstellar "amorphous silicates", leading to the suggestion that one of the fundamental building blocks of the solar system has been found within IDPs collected in the stratosphere (Bradley, 1994a; Bradley et al., 1999). The suggestion has stimulated debate among meteoriticists and astronomers because the proposal that GEMS are presolar was made without measuring their isotopic compositions (Flynn, 1994; Martin, 1995; Hoppe and Zinner, 2000; Ott, 2003). The only way to rigorously establish that grain is presolar is to measure non-solar isotopic compositions, although a solar isotopic composition does not rule out a presolar origin. (The isotopic compositions of galactic cosmic rays, thought to originate from shock-accelerated interstellar dust, are with few exceptions solar (Westphal and Bradley, 2004)). Non-solar oxygen isotopic abundances have been measured in several GEMS establishing their interstellar origins (Messenger et al., 2003; Floss et al., 2004). In addition, GEMS and/or the organic carbonaceous matter in which they are usually embedded were recently implicated as carriers of the astronomical ~2175 Å extinction feature (Bradley et al., 2005).

Analysis: Since GEMS are natural "nanomaterials" the devil truly is in the (analytical) details and deciphering their record requires painstaking long-term investigations. They are extremely fine-grained and heterogeneous down to the nanometer scale, significantly beyond the spatial resolution and detection limits of most analytical instruments. Only analytical transmission electron microscopy (TEM) offers the required probe-forming optics, spatial resolution and detection limits to measure individual constituents of GEMS, metal and sulfide nanocrystals, on a grain-by-grain basis. However, even TEM measurements are limited by the thickness of prepared specimens. Ideally sections for TEM should be ~1 monolayer of grains thick, i.e. 10 nm or less for GEMS whereas most sections of GEMS are 50-100 nm thick. Our understanding of the nature of GEMS-rich IDPs in general and GEMS in particular is constrained to an unusual degree by the capabilities of the instruments we are using to study them.

The analytical difficulties inherent in studying GEMS are reflected in the literature. Keller & Messenger (2005) propose that most GEMS originated in the inner solar nebula as high-temperature vapor phase condensates, and that they are closely related to the crystalline silicates in IDPs. Brownlee et al. (2005) observed that when GEMS are heated to ~700 C they undergo a sub-solidus transformation to an igneous-like texture. They conclude that GEMS must have a cold (<700 C) origin, they did not originate in the inner solar nebula, and that they are not related to the crystalline silicates in IDPs. Keller et al. (2002) describe GEMS with Mg-rich cores, and Keller & Messenger (2004) describe GEMS without Mg-rich cores. Some GEMS contain relict grains, while others do not (Bradley 1994a; Bradley & Dai 2004; Keller & Messenger 2004). Some GEMS have non-solar isotopic compositions, while others do not, although isotopic measurements are not yet precise enough to establish or rule out a presolar origin for most GEMS (Keller & Messenger 2005). S/Si, Mg/Si, Ca/Si and Fe/Si ratios in GEMS are systematically depleted with respect to solar abundances. Some suggest that the depletions rule out a presolar origin, while others suggest they favor of a presolar origin (Westphal & Bradley 2004; Keller & Messenger, 2004).

There is even confusion about which grains in IDPs are actually GEMS (see Rietmeijer 1998). Bradley (1994a) and Bradley & Dai (2004) propose that GEMS are pseudomorphic end members of a spectrum of related grains in IDPs, ranging from euhedral single-mineral crystals (e.g.,forsterite and pyrrhotite), to GEMS with embedded "relict" grains (e.g., forsterite and pyrrhotite crystals), to classical spheroidal glassy GEMS composed essentially of glass with embedded metal and sulfides. On the one hand the suggestion that other types of mineral grains in IDPs are related to GEMS complicates matters further, while on the other suggests that nanometer-scale mineralogical and petrographic heterogeneity of (GEMS-rich) IDPs is not as complicated as it appears to be. Clearly, there is much to learn about GEMS.

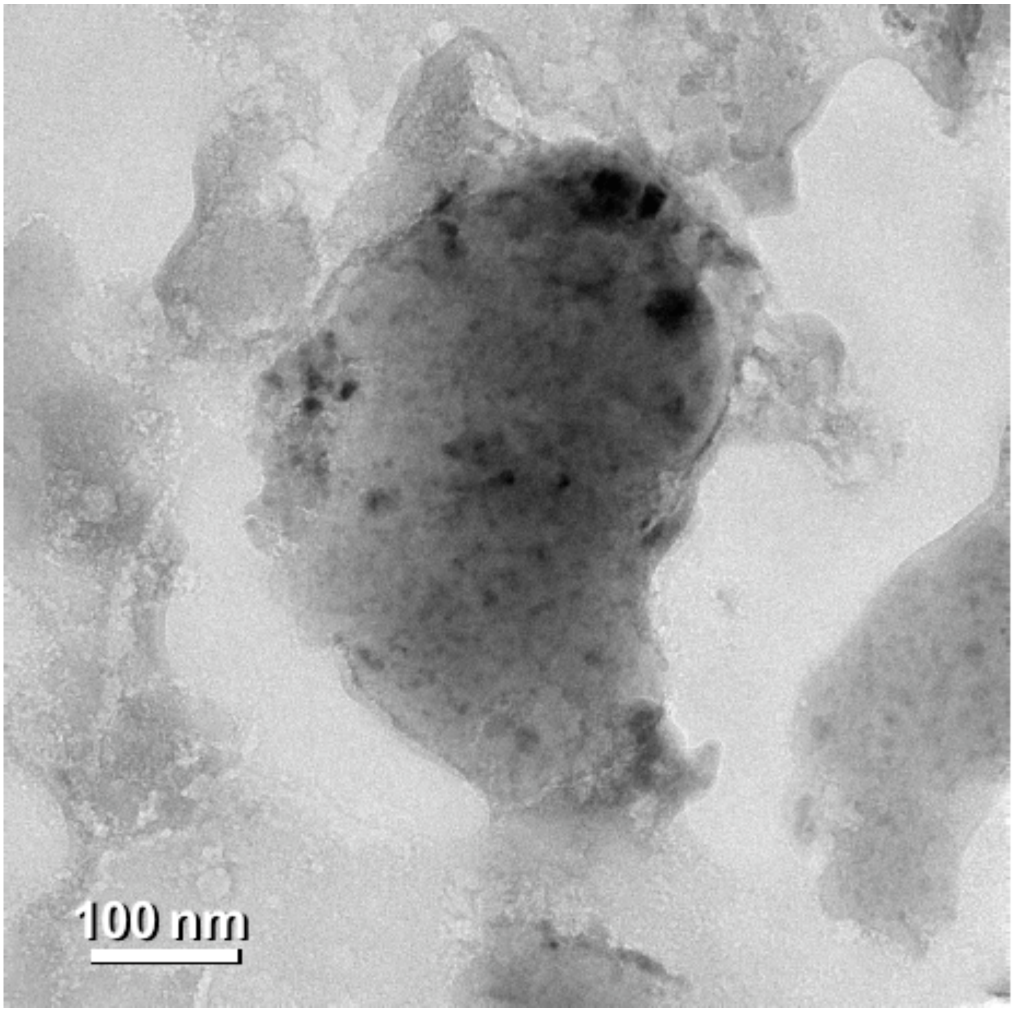

Fig. 1. GEMS in IDP "Butterfly". In addition to abundant GEMS, enrichments in D/H, in which δD varies between -200‰ and +2700‰, have been measured. Ion imaging of one fragment of "Butterfly" had an inferred δD of at least +9,000‰ (see Messenger et al. 1996).

State of preservation of GEMS: All IDPs are frictionally heated during atmospheric entry with (GEMS-rich) cometary IDPs captured from orbits with high eccentricities most likely to have been the severely heated (Love & Brownlee 1996; Brownlee et al. 1995). The crystalline silicates in IDPs often contain solar flare tracks, and in the absence of other indicators, it is generally assumed that tracks are indicative of a "pristine" IDP, because tracks are erased by heating above ~650°C (Bradley et al. 1984). Only Reitmeijer has systematically explored the effects of atmospheric entry heating and the "dynamic pyrometamorphism" that may occur during atmospheric entry (Rietmeijer 1998).

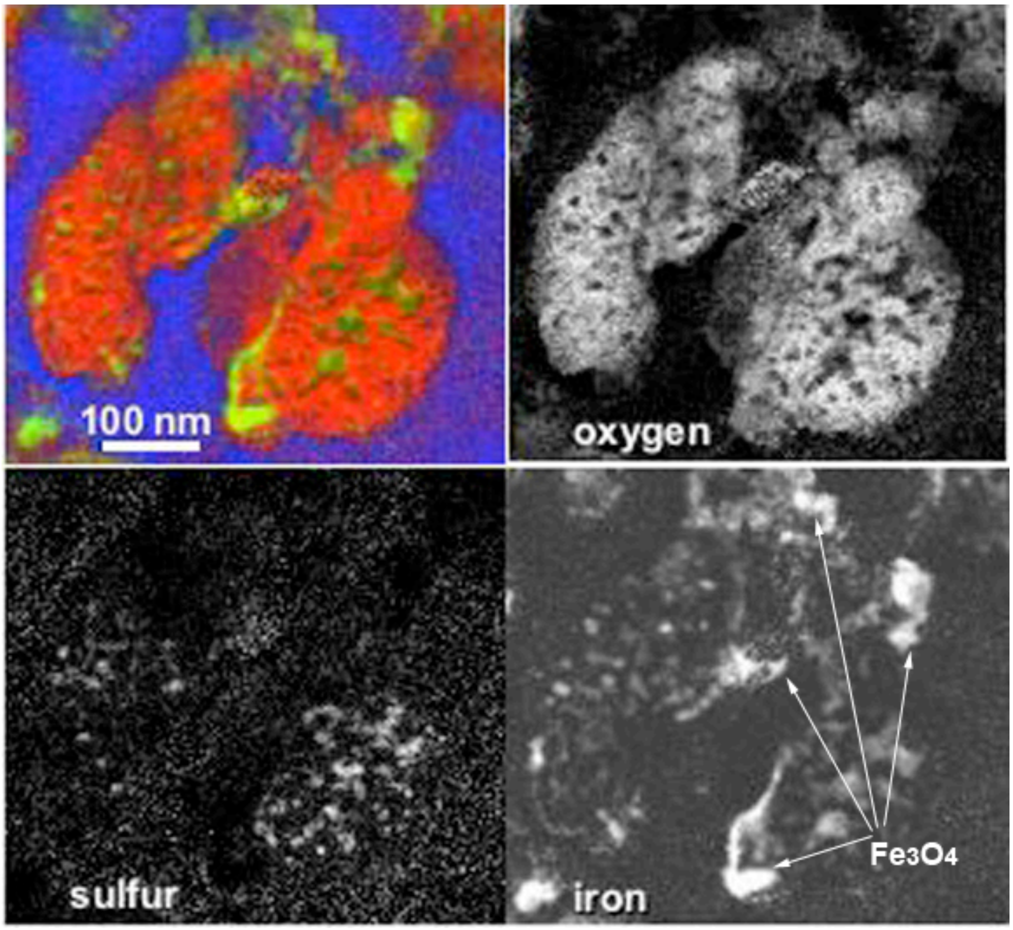

Fig. 2. Energy-filtered images showing the distribution of O, S and Fe in GEMS within IDP "Butterfly". The color image highlights the distribution of oxygen (red) in silicate glass and Fe^{3+} (yellow-green) in magnetite (Fe_3O_4).

Recent results underscore the limitations of solar flare tracks for assessing the thermal histories of IDPs. The latest generation TEMs offer the ability to obtain multi-element compositional maps with spatial resolution approaching ~1 nm. For the first time, the distribution of major elements relative to one another within the ultrafine-grained constituents of IDPs can be visualized. Figure 2 shows energy-filtered images of GEMS in IDP "Butterfly" (Bradley 1994b). Although "Butterfly" is an otherwise pristine IDP, as evidenced by solar flare tracks and D/H enrichments (Messenger et al. 1996), the presence of Fe^{3+}-rich rims on the surfaces of GEMS indicate that there has been significant nanoscale mobilization of Fe (and loss of S) as a result of (thermal) oxidation. Similar nanoscale rims are observed on the surfaces of other types of grains in "Butterfly" (Fig. 3). New metrics need to be identified to distinguish truly pristine GEMS from those that have been significantly modified by post-accretional processes (e.g., atmospheric entry).

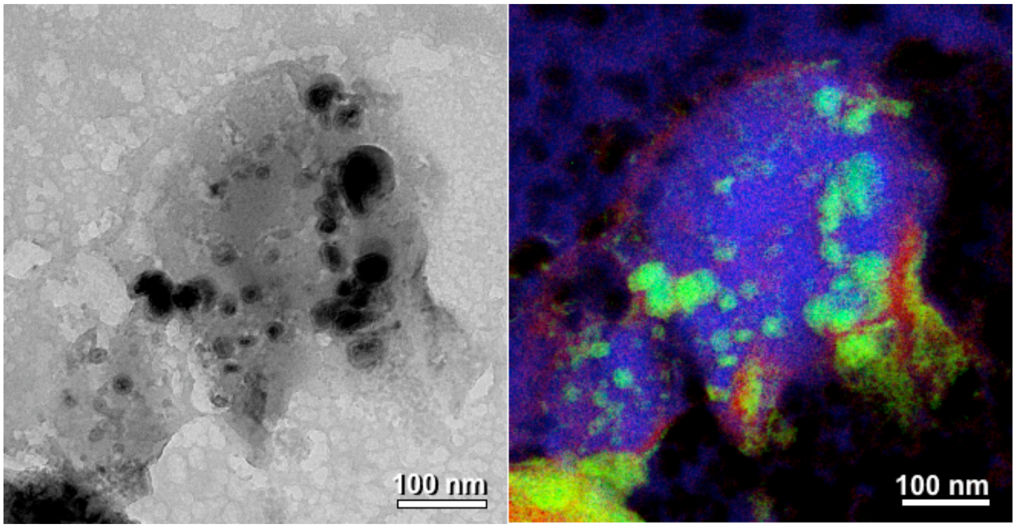

Fig. 3. (Left) Brightfield micrograph of a reduced aggregate in IDP "Butterfly". Although reduced aggregates are texturally similar to GEMS, their amorphous matrices are carbonaceous rather than silicate glass. The inclusions are FeNi metal (kamacite), FeNi carbide and Fe-rich sulfides (Bradley 1994b). (Right) Colorized energy-filtered image showing the distribution carbon (blue), FeNi sulfides plus FeNi metal (green), and Fe^{3+} plus O as magnetite (Fe_3O_4) (red).

GEMS are susceptible to modification by electron irradiation. This is an emerging problem because TEM's using high-brightness focused nanoprobes are increasingly being used to study IDPs and other fine-grained meteoritic materials. Figure 4 shows the effect of a 300 keV focused nanoprobe on crystalline forsterite. After ~1 second exposure the crystal structure is degraded (amorphized), and it is likely accompanied by significant nanoscale compositional changes.

Future directions: Nanoscale compositional mapping is assuming an important role in the largely unexplored area of IDP petrography (Figs. 2, 3, 5), as well as the petrography of other fine-grained meteoritic materials (Bradley & Dai 2004; Floss et al. 2004; Yada et al. 2005). Petrographic maps can be obtained using either energy-filtered imaging, x-ray mapping or both (Fig. 5). Energy-filtered imaging is the method of choice because of higher collection efficiency, rapid image acquisition (1-30 seconds), and high sensitivity for light elements (C, N & O). X-ray mapping suffers from low x-ray collection efficiency, extended data acquisition times (30-60 minutes), higher electron irradiation doses, and lower sensitivities for light elements (cf. Figs. 5b, f). Since a focused nanoprobe is required, sample degradation can be an issue (Fig. 4), and specimen drift compensation software is required because of the extended acquisition times. Highest spatial resolution x-ray maps are obtained at the expense of counting statistics (Fig. 5). Conversely, quantitative x-ray maps (those with good counting statistics) are obtained at the expense of spatial resolution. However, modern TEM's typically offer both energy-filtered imaging and x-ray mapping such that the strengths and limitations of each method can counterbalanced for maximum yield of information.

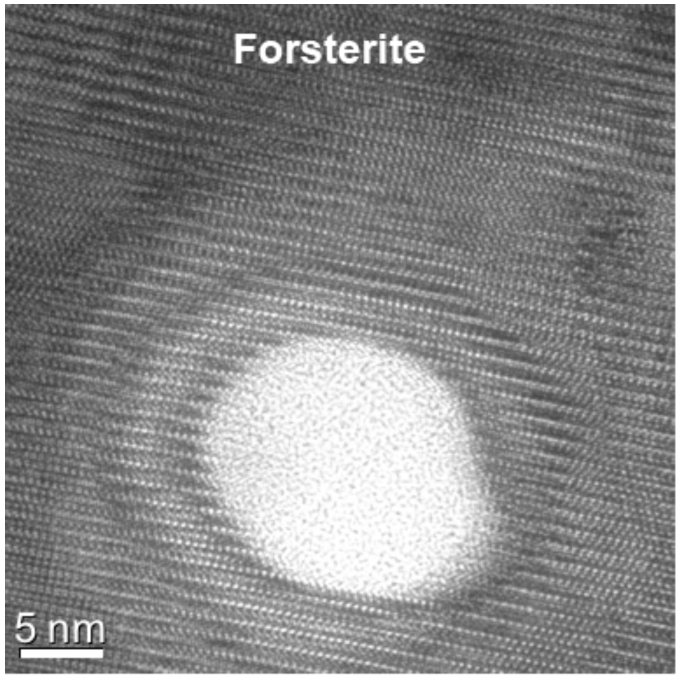

Fig. 4. Focused probe electron irradiation damage in a forsterite crystal.

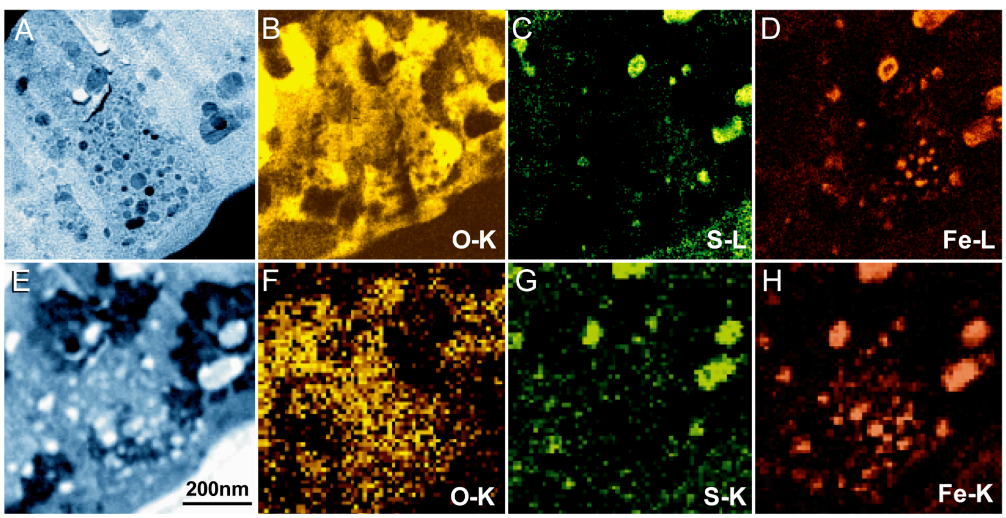

Fig. 5. Comparison of energy filtered TEM imaging (B, C & D) and X-ray mapping (F, G & H) from IDP L2036-G16. TEM sample was prepared by focused ion probe technique (Graham et al. 2004, 2005). (A) is a zero-loss filtered image, and (E) is the corresponding annular dark-field STEM image.

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